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IMPROVED PROCESS FOR THE PRODUCTION OF STAINLESS STEEL SUBSTRATES WITH CORROSION RESISTANT BLACK AND SHINING COATINGS."

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian Registered body incorporated under the Registration of Societies Act (Act XXI of 1860)

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

148034

This is an invention by Kummattithidal Santhanam RAJAGOPALAN, Subbiah Nadar GURUVIAH, Mrs VENU SUBRAMANIAN, Scientists, Venkatasubramanian CHANDRASEKARAN, Senior Scientific Assistant and Mrs VINAYALAKSHMI RAMAKRISHNAN, Senior Laboratory Assistant - all from Central Electrochemical Research Institute, Karaikudi - 623 006, Tamil Nadu, India and Indian citizens.

This invention relates to the improvements in or relating to the formation of a corrosion resistant black and shining coating of 2 micron thick on stainless steel of the type used in surgical tools (Cr = 12.14%, C = 0.25 - 0.3%, Si = 0.6%, Mn = 0.6%).

Hitherto several treatments for forming black oxide coatings on stainless steel have been reported

There are open to objection that these baths do not give a corrosion resistant, black shining coating on stainless steel of the type used in surgical tool (Table 1).

The object of the present invention is to work out suitable treatment procedure to get the desired results, namely, corrosion resistance, shiny black coatings on stainless steels of the type used in surgical tools.

To these ends of the invention broadly consists of

(a) mechanical polishing,

(b) degreasing in benzene or acetone,

(c) dipping for 1 to 5 minutes in 4 to 7 N Hydrochloric acid.

(d) dipping for 1/2 to 2 minutes in a mixture of concentrated acids consisting of HCl + HNO_3 + H_2SO_4 + H_2O taken in the ratio of 90 - 100 cc : 50 - 60 cc : 20 - 30 cc : 100 - 1000 cc.

(e) washing in water

(f) immersing in a bath containing KOH 280 - 300 gpl. HgO 0.5-1.0 gpl at 100 - 115°C. for 20 - 40 minutes.

(g) washing in water and

(h) drying in air

in which steps $ (a), (b) (e) (g) (h) are common to known processes and the new process, (c) gives the specific composition of pickling bath suitably to the present case and (d) gives the new step which in combination with (e) and (f) gives the new result, namely shiny black, corrosion resistant coating on stainless steel of the type used in surgical tools not obtained by the older processes.

TABLE 1 148034

VARIOUS TREATMENT TRIED TO PRODUCE A BLACK COATING ON SURGICAL STAINLESS STEEL

Sl.No.	Treatments	Remarks
1	The specimen was pickled, washed and immersed in 9 M H_2SO_4 + 1 M CrO_3 solution at 100°C for 15 minutes	The specimen was found to be attacked but no coating was formed
2	The specimen was pickled, washed then immersed in M-H_2SO_4 + 0.8 M CrO_3 at 65°C. for 25 minutes	No coating was formed.
3	The specimen was pickled, washed and then immersed in 1 : 1 H_2SO_4 containing 48% CrO_3 at 100°C. for 2 minutes	The specimen was found to be attacked.
4	After pre-treatment as above, the specimen was immersed in a solution containing H_2SO_4 (180 parts), H_2O (100 parts) $K_2Cr_2O_7$ (50 parts) at 100°C for 5-10 minutes.	The specimen was found to be attacked and the coating was very unsatisfactory.
5	The specimen was pickled, washed then immersed in aqueous solution containing 120% NaOH + $NaNO_3$ at 130-135°C for (a) 15 minutes, (b) 60 minutes.	The specimen was greyish in appearance after the treatment
6	NaOH 120% + $NaNO_3$ 30% + 1% $K_2Cr_2O_3$	Dull light grey in appearance
7	NaOH 55% + KOH 20% + $NaNO_3$ 10% + PbO_2 5%	Dull black coating is obtained
8	The specimen was pickled in the HCl, washed and dipped in 280 g.p.l. KOH + 500 mgpl HgO at 105-110°C for 5-10 minutes.	Dull black coating was obtained

TABLE 2 148034

Sl.No. Treatment (1) (2)	Colour and the coating. (3)	Thickness of the coating. (4)	Salt fog tests 5% NaCl. (5)	Conc., HNO_3 acid. (6)	Conc., H_2SO_4 (7)	Sterilization tests (8)
1. The specimen was pickled, washed and then immersed in a solution containing 250 gpl $K_2Cr_2O_7$ + 500 cc H_2SO_4, at 99°C.	Black	-	-	-		Failed.
2. The specimen was treated in HCl (1:1) and HCl + HNO_3 + H_2SO_4 mixture and immersed for 45 minutes in solution containing 530 gpl. NaOH + 200 gpl KOH + 100 gpl $NaNO_3$ + 50 gpl PbO_2 at 136-140°C.	Black	-	-	-		Failed.
3. The specimen was mechanically cleaned (using coarse emery paper) degreased and immersed in a bath containing 280 gpl KOH + 500 mgpl HgO, at 105½-110°C.	No coating formed.					
4. The specimen was pickled in 1:1 HCl. and immersed in the bath mentioned in 3 above.	-	"				
5. The specimen was treated in Clark's solution (Conc., HCl 250 g, Sb_2O_3 - 120 g, SnO_2 - 48 g) and immersed in the bath mentioned in 3 above.	-	"				
6. The specimen was pickled in Conc., HCl containing Sb_2O_3 & $SnCl_2$ in the ratio 10 (approx.) 5 : 2 and immersed in bath mentioned in 3 above.	-	"				

(continued)

TABLE 2 CONTINUED 148034

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
7.	The specimen was pickled in 1:3 H_2SO_4 and immersed in bath mentioned in 3 above.						
8.	The specimen was treated in 5N sulphuric acid solution and immersed in the bath mentioned in 3 above.		No coating formed.				
9.	The specimen was pickled in HNO_3 and immersed in the bath mentioned in 3 above.						
10.	The specimen was pickled in HCl + HNO_3(1:3) and immersed in bath mentioned in 3 above.						
11.	Treatment as mentioned in example.	Shiny Black	2.3+0.6 microns	Resists 6½ hours.	Resists.	Resists for several minutes.	

* Sterilization: Tests which consisted of 6 cycles of alternate boiling and cooling of distilled water in which the test sample was kept immersed. If no rust spots formed, the sample is taken as having passed the tests.

Typical example is given below:-

Example 1

Surgical tool received is treated as follows:-

(a) mechanically polished

(b) degreased in benzene

(c) pickled in 5.6 N HCl acid for 1-2 minutes

(d) dipped for 1/2-1 minute in concentrated HCl - Conc., HNO_3 - conc., H_2SO_4-H_2O mixture taken in the ratio of 4 : 2 : 1 : 4 by volume.

(e) washed with water

(f) immersed in a bath containing 280 gpl. KOH + 0.5 gpl HgO at ~~a~~ at 105°-110°C. for 30 minutes.

(g) washed in water and

(h) air dried.

Table 2 shows that out of several treatments which gave black oxide coating, only the coating obtained by the treatment described by Example 1 gives the desired corrosion resistance, thickness and appearance.

The main advantages of the invention are:-

(1) The treatment gives 2 micron thick black shining coating on stainless steel components used in surgical instruments.

(2) The treated surgical tool passes the sterilisation test.

~~Dated this 25th day of March, 1977.~~

Dated The 17th day of August, 1977.

Asstt. Patents Officer,
Council of Scientific & Industrial Research

148034

THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10) .

IMPROVED PROCESS FOR THE PRODUCTION OF STAINLESS STEEL SUBSTRATES WITH CORROSION RESISTANT BLACK AND SHINING COATINGS.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH Rafi Marg, New Delhi-1, India, an Indian Registered body incorporated under the Registration of Societies Act (Act XXI of 1860)

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This is an invention by Kummattithidal Santhanam RAJAGOPALAN, Subbiah Nadar GURUVIAH, Mrs. Venu Subramanian, Scientist, Venkatasubramanian CHANDRASEKHARAN, Senior Scientific Assistant and Mrs. Vijayalakshmi RAMAKRISHNAN, Senior Laboratory Assistant all from Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India and Indian citizens.

This invention relates to an improved process for the production of stainless steel substrates with corrosion resistant black and shining coatings. The stainless steel substrates used may be of the type used in surgical tools (Cr=12-14%, C=0.25-0.3%, Si=0.6%, Mn=0.6%).

Hitherto several processes for forming black oxide coatings on stainless steel have been reported particularly treating the substrate in acid and alkaline bath as given in detail in tables I & II.

These are open to the objection that these do not give corrosion resistant black shining coating or any coating at all on stainless steel of the type used in surgical tool (Table 1).

The main object of the present invention is to develop an improved process to get the desired results, namely corrosion resistance, shiny black coatings on stainless steel of the type used in surgical tools.

The other objectives of the invention are :
to develop a process which gives at least a 2 micron thick black shining coatings on stainless steel substrates used in the manufacture of surgical instruments.

Table 2 shows in comparison that out of several processes which gave black oxide coating, the coating obtained by the process of para 11 of table II and described in example 1 only gives the desired thickness, corrosion resistance and appearance.

Accordingly this invention provides an improved process for the production of stainless steel substrates with corrosion resistant black and a shining coatings comprising treatment of the substrates in an acid bath and further in an alkaline bath, characterised in that the sequence of steps of the process are : mechanically polishing the substrate, degreasing the same with an organic solvent, pickling the same in a mineral

acid, treating the pickled substrate in a concentrated acid bath, washing the substrate with water, further treating the washed substrate in an alkaline bath and washing the thus treated substrate with water and drying the same.

According to another feature of the invention the acid bath used may consist of an admixture of mineral acids such as hydrochloric acid, sulphuric acid and nitric acid.

According to a further feature of the invention the alkaline bath used may consist of an admixture of potassium hydroxide and mercury oxide. The process of the present invention thus consists of steps of subjecting the substrate (a) mechanical polishing, (b) degreasing in benzene or acetone, (c) dipping for 1-5 minutes in 4 to 7N HCl, (d) dipping for 2 minutes to 30 minutes in a mixture of concentreated acids consisting of HCl + HNO_3 + H_2SO_4 + H_2O taken is the ratio of 90-100 c.c. 50-60 c.c. 20-50 c.c. 100-1000 c.c., (e) washing it in water, (f) immersing in a bath containing KOH-280-300 g/l of water, HgO 0.5-1.0 g/l of water at 100-115°C for 20-40 minutes, (g) washing in water, and (h) drying in air. This process gives shiny black, corrosion resistant coatings on stainless steel substrates of the type used in surgical tools not obtained by the known processes.

The main feature of the invention thus is that when the substrates, a surgical tool is degreased in acetone, cleaned in 4-7N HCl dipping in concentrated and mixture of HCl, HNO_3, H_2SO_4, H_2O in the ratio of 4 : 2 : 1 : 4 by volume followed by rinsing= in water and dipping in bath containing 280-300 g/l KOH and 0.5 to 1 g/l HgO at 100-115°C for 30 minutes, a shining back corrosion resistant coating is formed on the surgical tools. The black shining coating is obtained after immersing the alkaline both. The pre-treatment surgical tools step is necessary to get the black shining coatings.

Example-1

Surgical tool formed of stainless steel is treated as follows :

1. Mechanically polished,
2. Degreased in benzene,
3. Pickled in HCl 5-6

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4. Dipped in conc., acid for 1 minute - HCl : HNO_3 : H_2SO_4 : H_2O 4 : 2 : 1 : 4 by volume.

5. Washed in water.

6. Immersed in bath containing 280 g/l KOH + 0.5 g/l HgO at $115^{\circ} + 5^{\circ}$ C for 1/2 an hour.

7. Washed in water and dried to obtain black shining coating on the tool.

It has thus shown that a black shining corrosion resistant black coating on stainless steel used for surgical tool is obtained by the process of this invention described above.

TABLE 1 148034

VARIOUS TREATMENT TRIED TO PRODUCE A BLACK COATED ON SURGICAL STAINLESS STEEL

Sl.No.	Treatments	Remarks
1	The specimen was washed, pickled and immersed in 9M H_2SO_4 + 1M CrO_3 solution at 100°C for 15 minutes	The specimen was found to be attacked but no coating was formed.
2	The specimen was pickled, washed then immersed in M H_2SO_4 + 0.8 M CrO_3 at 65°C for 25 minutes	No coating was formed.
3	The specimen was pickled, washed and then immersed in 1:1 H_2SO_4 containing 48% CrO_3 at 100°C for 2 minutes.	The specimen was found to be attacked.
4	After pre-treatment as above, the specimen was immersed in a solution containing H_2SO_4 (180 parts) H_2O (100 parts) $K_2Cr_2O_7$ (50 parts) at 100°C for 5 - 10 minutes.	The specimen was found to be attacked and the coating was very unsatisfactory.
5	The specimen was pickled, washed then immersed in aqueous solution containing 120% NaOH + $NaNO_3$ at 130-135°C for (a) 15 minutes, (b) 60 minutes.	The specimen was greyish in appearance after the treatment.
6	NaOH 120% + $NaNO_3$ 30% + 1% $K_2Cr_2O_7$	Dull light grey in appearance
7	NaOH 55% + KOH 20% + $NaNO_3$ 10% + PbO_2 5%	Dull black coating is obtained
8	The specimen was pickled in the HCl, washed and dipped in 280 gpl KOH + 500 mgpl HgO at 105-110°C for 5 - 10 minutes.	Dull black coating was obtained

TABLE 2 148034

Sl.No.	Treatment	Colour and the coating	Thickness of the coating	Salt fog tests 5%NaCl	Conc., HNO_3 acid	Conc., H_2SO_4	Sterilisation Tests.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	The specimen was pickled in HCl, washed and then immersed in a solution containing 250 gpl $K_2Cr_2O_7$ + 500 cc H_2SO_4, at 99°C	Black	-	-	-	-	Failed
2	The specimen was treated in HCl (1:1) black and $HCl+HNO_3+H_2SO_4$ mixture and immersed for 45 minutes in solution containing 530 gpl. NaOH + 200 gpl KOH + 100 gpl $NaNO_3$ + 50 gpl PbO_2 at 136-140°C	Black	-	-	-	-	Failed
3	The specimen was mechanically cleaned (using coarse emery paper) degreased and immersed in a bath containing 280 gpl KOH + 500 mgpl HgO, at 105-110°C	No Coating Formed			-	-	-
4	The specimen was pickled in 1:1 HCl and immersed in the bath mentioned in 3 above	"	"	"	-	-	-
5	The specimen was treated in Clark' solution (Conc., HCl 2250 g, Sb_2O_3 - 120 g, SnO_2 - 48 g) and immersed in the bath mentioned in 3 above.	"	"	"	-	-	-
6	The specimen was pickled in Conc. HCl containing Sb_2O_3 & $SnCl_2$ in the ratio 10 (approx.) 5:2 and immersed in bath mentioned in 3 above.	"	"	"	-	-	-

(continued)

TABLE 2 (continued) 148034

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
7	The specimen was pickled in 1:3 H_2SO_4 and immersed in bath mentioned in 3 above	No Coating Formed	-	-	-	-	
8	The specimen was treated in 5N sulphuric acid solution and immersed in the bath mentioned in 3 above		-do-	-	-	-	
9	The specimen was pickled in HNO_3 and immersed in the bath mentioned in 3 above		-do-	-	-	-	
10	The specimen was pickled in HCl + HNO_3 (1:3) and immersed in bath mentioned in 3 above		-do-	-	-	-	
11	Treatment as mentioned in example	Shiny Black	2.3 + 0.6 microns	Resists 6½ hours	Resists	Resists for several minutes	Passes

*Sterilization: Tests which consisted of 6 cycles of alternate boiling and cooling of distilled water in which the test sample was kept immersed. If no rust spots formed, the sample is taken as having passed the tests.

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We Claim :

1. An improved process for the production of stainless steel substrates with corrosion resistant black and shining coatings comprising treating the substrates in an acid bath and further in an alkaline bath, characterised in that the sequence of steps of the process are : mechanically polishing the substrates, degreasing the same with an organic solvent, pickling the same in a mineral acid, treating the pickled substrate in a concentrated acid bath, washing the substrate with water, further treating the washed substrate in an alkaline bath and washing the thus treated substrate with water and drying the same.

2. Process as claimed in claim 1 wherein the acid bath consists of an admixture of mineral acids such as hydrochloric acid, sulphuric acid and nitric acid.

3. Process as claimed in claim 1 wherein the alkaline bath consists of an admixture of potassium hydroxide and mercury oxide.

4. Process as claimed in claim 1-3 wherein the substrate is mechanically polished, degreased in benzene or acetone, pickled in 4-7N HCl, dipped in concentrated acid admixture of HCl: HNO_3 : H_2SO_4 : H_2O in the ratio of 4 : 2 : 1 : 4 by volume, washed in water, immersed in the alkaline bath containing 280-300 g/l of KOH in water and 0.5 to 1 g/l of HgO in water at 100-115°C, washing with water and drying the coated substrate.

5. Process as claimed in any of the preceding claims wherein the substrate is treated in the acid admixture for 2 to 30 minutes and immersed in the alkaline bath for 20 to 40 minutes.

6. Process as claimed in claim 5 wherein the substrate is treated in the alkali bath containing 280 g/l of KOH and 0.5 g/l of HgO at 115°C + 5°C for 30 minutes.

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7. Improved process for the production of stainless steel substrates with corrosion resistant black and shining coatings substantially as herein described.

Dated this 9th day of August, 1978.

(I. M. S. MAMAK)
SCIENTIST 'E' (PATENTS)
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

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